

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 414 228 A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90116097.8

(51) Int. Cl.⁵: C11D 3/37

(22) Date of filing: 22.08.90

(30) Priority: 25.08.89 JP 217534/89

(43) Date of publication of application:
27.02.91 Bulletin 91/09

(84) Designated Contracting States:
CH DE FR GB LI

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(54) Washability improver for textile article.

(57) A washability improver for a textile article, which comprises a reaction product obtained by radical polymerization of at least one monomer selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and salts thereof in the presence of poly- α -hydroxyacrylic acid or a salt thereof. The washability improver attains excellent dispersibility-improving, washability-improving, and metal-removing effects and prevents a soil deposition on fibers and machines and a formation of scales.

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WASHABILITY IMPROVER FOR TEXTILE ARTICLE

BACKGROUND OF THE INVENTION

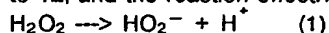
(1) Field of the Invention

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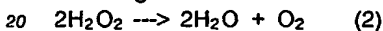
The present invention relates to a washability improver for a textile article. More particularly, the present invention relates to a washability improver for a textile article, which has a high alkali resistance and is used at the steps of desizing, scouring, bleaching or soaping cellulose fibers such as cotton and flax, synthetic fibers such as polyester, nylon and acrylic fibers, and mixed fibers thereof, mercerizing cotton, alkali-reducing polyester fibers, and washing a dyeing bag.

(2) Description of the Related Art

15 Bleaching by hydrogen peroxide is generally carried out under an alkaline condition of a pH value of 10 to 12, and the reaction effectively improving the whiteness is expressed by the following formula:



Under an alkaline condition (pH value of at least 10), however, the side reaction represented by the following formula:



is promoted by ions of heavy metals contained in cellulose fibers of cotton, flax or the like, and in a bleaching bath, such as iron, calcium, copper and manganese, and therefore, as is well-known, the whiteness is not increased and the fibers are made brittle.

To eliminate this disadvantage, sodium silicate is frequently used as the stabilizer, but the use of 25 sodium silicate is disadvantageous in that water-insoluble salts of calcium and magnesium, i.e., silicate scales, are formed, and these insoluble salts adhere to and are deposited on a bleached article and a bleaching apparatus to cause a silicate problem.

As stabilizers other than sodium silicate, there are known organic chelating agents such as EDTA and DTPA, inorganic chelating agents such as condensed phosphates, and water-soluble proteins such as 30 soybean protein and casein (Japanese Examined Patent Publication No. 50-34675). These stabilizers do not cause a silicate problem in the batchwise method, but in the continuous method, the stabilizing effect attained by these stabilizers is much lower than the effect attained by sodium silicate and satisfactory results cannot be obtained if the operation is carried out on an industrial scale.

It has been confirmed that a stabilizer comprising, as the main ingredient, a salt of poly- α -hydrox- 35 yacrylic acid, for example, Neorate PLC-700 (supplied by Nikka Chemical) (Japanese Unexamined Patent Publication No. 62-185797), has an excellent stabilizing effect, gives a whiteness comparable to that given by sodium silicate, and does not cause a silicate problem.

Furthermore, there has recently been adopted a process in which, at the steps of desizing, scouring, bleaching or soaping cellulose fibers, mercerizing cotton, alkali-reducing polyester fibers and washing a 40 dyeing bag, a chelating agent such as EDTA or DTPA or a polycarboxylic acid such as sodium polyacrylate or sodium polymethacrylate is used, to increase the washing efficiency.

In general, most non-silicate type hydrogen peroxide stabilizers, other than sodium silicate, have a poor stabilizing effect, and the alkali-resistant stability of stock solutions is low.

Polysphosphoric acid salts such as sodium tripolyphosphate, and aminocarboxylate type organic chelat- 45 ing agents such as ethylenediamine-tetraacetic acid (EDTA) and diethylenetriamine-pentaacetic acid (DTPA), which are used at the steps of desizing, scouring, bleaching and soaping cellulose fibers, mercerizing cotton, alkali-reducing polyester fibers and washing a dyeing bag, are disadvantageous in that, in a region of high pH values, the chelating capacity is reduced, the chelating agents are insolubilized in the presence of an excessive amount of a hardness component, to reduce the chelating effect, and scales are 50 formed by the hydrolysis. Accordingly, satisfactory results cannot be obtained.

In the case of polycarboxylic acids such as sodium polyacrylate and sodium polymethacrylate, the washing efficiency differs according to the degree of polymerization, and it is known that the effect of the selective adsorption in the continuous treatment varies widely.

SUMMARY OF THE INVENTION

The object of the present invention is to overcome the foregoing defects of the conventional techniques. More specifically, in accordance with the present invention, there is provided a washability improver for a textile article, which comprises a reaction product obtained by radical polymerization of at least one monomer selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and salts thereof in the presence of poly- α -hydroxyacrylic acid or a salt thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The washability improver of the present invention is formed by radical-polymerizing at least one member selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and acid and salts thereof in the presence of poly- α -hydroxyacrylic acid or a salt thereof.

The poly- α -hydroxyacrylic acid or salt thereof used in the present invention may be a depolymerization product thereof. Preferably, the molecular weight of the poly- α -hydroxyacrylic acid or salt thereof is 500 to 1,000,000, most preferably 1,000 to 100,000. The depolymerization can be effected with a radical initiator such as hydrogen peroxide or a persulfate.

As the salt of poly- α -hydroxyacrylic acid, preferably water-soluble salts such as sodium, potassium, ammonium, monoethanolamine and diethanolamine salts are used.

Furthermore, as the salt of acrylic acid, methacrylic acid or maleic acid, preferably water-soluble salts such as sodium, potassium, ammonium, monoethanolamine and diethanolamine salts are used.

The polymerization is carried out in the presence of a free-radical initiator. As the initiator, preferably persulfates such as potassium persulfate, sodium persulfate and ammonium persulfate, redox type initiators such as a combination of a persulfate and sodium bisulfite, hydrogen peroxide, and water-soluble azo type initiators are used. Preferably, the initiator is used in an amount of 0.1 to 1.0 part by weight per 100 parts by weight of the monomeric acid or the salt thereof.

Preferably, the poly- α -hydroxyacrylic acid or the salt thereof, and acrylic acid, methacrylic acid, maleic acid or the salt thereof are used at a weight ratio of from 10/1 to 1/10.

The polymerization temperature and time are preferably 50 to 90 °C and 2 to 5 hours.

The polymerization is preferably carried out by using an aqueous solution of the poly- α -hydroxyacrylic acid or the salt thereof as a medium. A water-miscible solvent can be added to this aqueous solution, if necessary.

The degree of polymerization can be effectively adjusted by using a chain transfer agent such as octyl thioglycolate.

The concentration of the washability improver is at least 0.05 g/l, preferably at least 0.2 g/l, as a product having a solid content of 20%.

When the washability improver of the present invention is used as a stabilizer for the hydrogen peroxide bleaching, batchwise apparatuses such as a wince dyeing machine, a jet dyeing machine and a cheese dyeing machine, and continuous apparatuses such as a J-box, an L-box and a purple range can be used as the bleaching machine. When the washability improver is used for scouring and soaping, a wince dyeing machine, a jet dyeing machine, a cheese dyeing machine, a jigger dyeing machine, a washer, an open soaper, and a relaxer can be used.

Where the washability improver is used for the mercerization of cotton or flax, the washability improver can be incorporated into a mercerizing bath or soaping bath of a yarn mercerizing machine or a knitted or woven fabric mercerizing machine. When the washability improver is used for the alkali reduction of polyester fibers, the washability improver can be incorporated into a reduction bath or soaping bath of a hanging, pad steam or cold pad batch, and when the washability improver is used for washing a dyeing bath, a jet dyeing machine, a beam dyeing machine, a cheese dyeing machine, and an Over maier dyeing machine can be used.

When the washability improver of the present invention is used at the steps of desizing, scouring and bleaching cellulose fibers, not only a hydrogen peroxide-stabilizing effect but also a high decomposition-promoting effect can be attained, and an abnormal decomposition by metal ions such as iron, copper and calcium ions can be controlled. Furthermore, a good dispersibility is given to decomposition products and a re-deposition of decomposition products can be prevented.

When the washability improver of the present invention is used at usual scouring and soaping steps, the dispersibility of a sizing agent, an oiling agent, an unfixed dye, and various scums is improved, and good results can be obtained at subsequent dyeing and finishing steps.

When the washability improver is used at the step of mercerizing cotton and flax, since the alkali resistance of the washability improver is good, a decomposition or separation of the washability improver per se does not occur, the deposition of scales on a roll or the like is prevented, and the dispersibility of the bath is improved.

5 When the washability improver of the present invention is used for the alkali reduction of polyester fibers, the effect of removing a polyester oligomer, titanium oxide and the like by washing is enhanced and a good touch can be obtained, and level dyeing can be attained at the subsequent dyeing step.

When the washability improver is used at the step of washing a dyeing bag, an effect of improving the dispersibility of a polyester oligomer, a dye complex, various scums and the like can be attained.

10 Where the hardness of the water is high, cotton or flax having high contents of metals carried by fibers is scoured or bleached or a high alkali concentration is adopted as in the mercerization of cotton or the alkali reduction of polyester fibers, by using the washability improver of the present invention, excellent dispersibility-improving, washability-improving, and metalremoving effects can be attained, and a soil deposition on fibers and machines and the formation of scales can be prevented. Furthermore, even where
15 the washability improver of the present invention is used for a continuous treatment, the bath stability is good and a satisfactory effect is obtained, and the treatment can be performed at a high efficiency and a high quality can be given to the product.

The present invention will now be described in detail with reference to the following examples, that by no means limit the scope of the invention.

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Synthesis Example 1

In a four-neck flask having an inner volume of 500 ml, 45 g (calculated as solids) of sodium poly- α -hydroxyacrylate was diluted with water so that the total amount was 200 g, and the temperature was
25 elevated to 75 °C, and 100 g of a monomer liquid formed by adding 15 g of a monomer of sodium acrylate and 0.02 g of potassium persulfate to water was added dropwise over a period of 30 minutes. Then polymerization was carried out at 80 to 85 °C for 3 hours and the reaction mixture was cooled to obtain about 300 g of a brown transparent liquid having a viscosity of 20 cp (referred to as "product 1 of the
30 present invention" hereinafter).

Synthesis Example 2

35 In a four-neck flask having an inner volume of 500 ml, 30 g (as solids) of sodium poly- α -hydroxyacrylate was diluted so that the total amount was 200 g, and the temperature was elevated to 75 °C, and 100 g of a monomer liquid formed by adding 30 g of a monomer of sodium methacrylate, 0.03 g of ammonium persulfate and 0.04 g of octyl thioglycolate to water was added dropwise over a period of 30 minutes. Then
40 polymerization was carried out at 80 to 85 °C for 3 hours and the reaction mixture was cooled to obtain about 300 g of a yellow transparent liquid having a viscosity of 50 cp (referred to as "product 2 of the present invention" hereinafter).

Comparative Example 1

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Diluted with water were 15 g (as solids) of sodium poly- α -hydroxyacrylate and 5 g (as solids) of sodium polyacrylate (having a molecular weight of about 5,000) so that the total amount was about 100 g, whereby
100 g of a brown transparent liquid having a viscosity of 45 cp (referred to as "comparative product 1" hereinafter) was obtained.

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Comparative Example 2

Diluted with water was 20 g (as solids) of sodium polyacrylate (having a molecular weight of about
55 5,000) so that the total amount was 100 g, whereby a light yellow transparent liquid having a viscosity of 160 cp (referred to as "comparative product 2" hereinafter) was obtained.

Comparative Example 3

Diluted with water was 20 g of tetrasodium ethylenediamine-tetraacetate (EDTA-4Na) so that the total amount was 100 g, whereby a light yellow transparent liquid having a viscosity of 5 cp (referred to as "comparative product 3" hereinafter) was obtained.

Performance Test Example 1 (Alkali Resistance)

A bath comprising x g/l of NaOH (flake) and 10 g/l of a sample was allowed to stand at room temperature for 24 hours, and the stability and alkali resistance were evaluated based on the degree of the formation of precipitates and the presence or absence of surface separation. The results are shown in Table 1.

Table 1

Sample	Stability			
	Amount (x) of NaOH			
	10 g/l	50 g/l	100 g/l	200 g/l
product 1 of the present invention	o	o	o	o
product 2 of the present invention	o	o	o	o
comparative product 1	⊠	x	x	x
comparative product 2	o	o	o	⊠
comparative product 3	o	o	o	⊠
Note				
o : stable				
⊠ : slight separation				
x : complete separation				

The polymer blend of sodium poly- α -hydroxyacrylate and sodium polyacrylate has an inferior alkali resistance, but the product of the present invention has a good alkali resistance and shows a stable compatibility even under such a high alkali concentration condition as adopted at the mercerization of cotton or the alkali reduction of polyester fibers.

Performance Test Example 2 (Hydrogen Peroxide-Stabilizing Effect)

A bleaching liquid comprising 30 cc/l of 35% H_2O_2 , 7 g/l of NaOH, 0.1 g/l of $MgSO_4 \cdot 7H_2O$, 2 ppm of Fe^{2+} and 5 g/l of a sample was prepared and the bleaching treatment was carried out at 95 °C for 30 minutes, the residual amount of hydrogen peroxide was determined according to the oxidation-reduction titration method, and the residual ratio (%) was calculated. The results are shown in Table 2.

Table 2

Sample	H ₂ O ₂ Residual Ratio (%)
product 1 of the present invention	78
product 2 of the present invention	70
comparative product 1	75
comparative product 2	0
comparative product 3	3
blank	2

The product of the present invention has a very good hydrogen peroxide-stabilizing effect and is especially preferably useful for continuous bleaching. In contrast, the sodium carboxylate and the chelating agent EDTA have no stabilizing effect.

Performance Test Example 3 (Whiteness)

A green cotton woven fabric (desized) was padded in a bleaching liquid comprising 30 cc/l of 35% H₂O₂, 4 g/l of NaOH (flake), 2 g/l of Sunmorl CS-1 (scouring penetrant supplied by Nikka Chemical) and 3 g/l of a sample, and the bleaching was carried out at 95 °C for 30 minutes by the pad steam method. The whiteness was evaluated by measuring the reflectance at 440 mμ by using a colorimeter, Macbeth MS-2020. The results are shown in Table 3.

Table 3

Sample	Whiteness (%)
product 1 of the present invention	75.5
product 2 of the present invention	74.8
comparative product 1	75.4
comparative product 2	72.1
comparative product 3	72.8
blank	71.9
Note, the whiteness of the starting fabric was 56.3%.	

The product of the present invention gives a greater whiteness than the sodium polycarboxylate and the chelating agent.

Performance Test Example 4 (Polyester-Scouring Effect)

Two drops each of 20% solutions of a commercially available sizing agent (Prassize J-97 supplied by Goo Kagaku) and a Poval sizing agent (PVA-205 supplied by Kuraray; saponification degree = 88%) were spotted on a polyester woven fabric (pongee), and setting was carried out at 180 °C for 30 seconds. Then, the polyester fabric was scoured at 90 °C for 5 minutes with a scouring solution comprising 1 g/l of Sunmorl BL-600 (scouring agent for synthetic fibers supplied by Nikka Chemical), 0.5 g/l of NaOH (flake), and 1 g/l of a sample. Then, the fabric was immersed in a dyeing bath containing 0.2 g/l of a disperse dye (Dianix Blue AC-E supplied by Mitsubishi Kasei), which had the pH value adjusted to 4. The temperature was elevated and dyeing was carried out at 70 °C for 5 minutes, and the scouring property (uneven dyeing and edge staining) was examined. The results are shown in Table 4.

Table 4

Sample	Scouring Property	
	Acrylic Sizing Agent	Poval Sizing Agent
product 1 of the present invention	o - □	o
product 2 of the present invention	o	o
comparative product 1	□ - o	o - □
comparative product 2	o	o - □
comparative product 3		o
blank (no additive)	□ - o	□
<u>Note</u>		
o : good		
□ : medial		

When the product of the present invention is used in combination with a scouring agent for synthetic fibers, the scouring property is improved.

Performance Test Example 5 (Cotton-Scouring Effect)

Two drops of a commercially available knitting oil (Bexilar A supplied by Showa Shell Sekiyu) were spotted on a scoured and bleached cotton knitted fabric, and the fabric was dried at 120 °C for 5 minutes and scoured at 90 °C for 5 minutes with a scouring solution containing, 1 g/l of Sunmorl BH Conc. F (cotton scouring agent supplied by Nikka Chemical), 1 g/l of Na₂CO₃ and 1 g/l of a sample. Then, the fabric was immersed in a dyeing bath containing 0.1 g/l of a direct dye (Kayarus Supra Ilue BWL supplied by Nippon Kayaku). The temperature was elevated and dyeing was carried out at 60 °C for 5 minutes. The scouring property (uneven dyeing and edge staining) was examined. The results are shown in Table 5.

Table 5

Sample	Scouring Property
product 1 of the present invention	o - □
product 2 of the present invention	o - □
comparative product 1	□ - o
comparative product 2	o - □
comparative product 3	□ - o
blank (no additive)	□
<u>Note</u>	
o : good	
□ : medial	

Performance Test Example 6 (Soaping Effect-Improving Capacity)

A cotton broadcloth printed with a reactive dye was soaped at 95 °C for 15 minutes with a soaping solution comprising 1 g/l of Lipotol RK-S (soaping agent for reactive dyes supplied by Nikka Chemical) and 1 g/l of a sample. The staining of the white area of the print was checked by using a gray scale. The results

are shown in Table 6.

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Table 6

	Staining (class) of White Area		
	Reactive Dye		
Sample	Diamira Turg. Blue B (supplied by Mitsubishi Kasei), 3%	Diamira Black B (supplied by Mitsubishi Kasei), 7 %	Sumifix Brill. Red 78F (supplied by Sumitomo Kagaku), 3%
product 1 of the present invention	5	5	5
product 2 of the present invention	5	5	5
comparative product 1	5	5	4-5
comparative product 2	4-5	4	4
comparative product 3	5	5	5
blank (Lipitol RK-S alone)	3-4	3-4	3-4
blank	3	3	3

The product of the present invention has a soaping effect-improving capacity. The comparative product 3 (chelating agent, EDTA-4Na) is discolored by the dyes.

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Performance Test Example 7 (Alkali Reduction of Polyester)

A polyester pongee was immersed at a bath ratio of about 1/30 in an alkali-reducing bath comprising 30 g/l of NaOH and 1 g/l of a sample and the hanging alkali reduction was carried out at 95 °C for 2 hours. The turbidity of the reducing bath was visually judged, the reduction ratio was determined and the touch was evaluated. The results are shown in Table 7.

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The comparative product 1 was not tested because the alkali resistance was poor.

Table 7

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Sample	Turbidity of Reducing Bath	Reduction Ratio (%)	Touch
product 1 of the present invention	o	9.2	o
product 2 of the invention	o	9.0	o
comparative product 2	□	8.0	o - □
comparative product 3	o	8.8	o
blank	x	8.9	o - □
<u>Note</u>			
Turbidity			
o: transparent			
□: opaque			
x: scums present			
Touch			
o: good			
□: medical			

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The product of the present invention has a good alkali resistance and an excellent dispersibility, and does not inhibit the alkali reduction.

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Performance Test Example 8 (Dyeing Bag-Washing Effect-Improving Capacity)

To check the property of dispersing a dye scum (disperse dye/cationic dye complex) and a polyester fiber oligomer scum, a liquid comprising 0.1 g/l of scums, 1 g/l of Sunmorl DMC (bag detergent supplied by Nikka Chemical), 2 g/l of sodium hydrosulfite, 2 g/l of NaOH (flake) and 2 g/l of a sample was treated at 130 °C for 45 minutes (by using Minicolor supplied by Texam Giken), and the liquid was filtered at 90 °C and the presence or subsence of the residue was checked. The results are shown in Table 8.

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Table 8

Sample	Dispersibility	
	Dye Complex Scum	Oligomer Scum
product 1 of the present invention	o	o - □
product 2 of the present invention	o	o
comparative product 1		□ - o
comparative product 2	o - □	o - □
comparative product 3	o	o
blank	x	x
Note		
o: no scum		
□: slight amount of scum		
x: considerable amount of scum		

The product of the present invention has a scum dispersion-promoting effect.

Claims

1. A washability improver for a textile article, which comprises a reaction product obtained by a radical polymerization of at least one monomer selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and salts thereof in the presence of poly- α -hydroxyacrylic acid or a salt thereof.
2. A washability improver as set forth in claim 1, wherein the poly- α -hydroxyacrylic acid or salt thereof has a molecular weight of 500 to 1,000,000.
3. A washability improver as set forth in claim 1, wherein the salt of poly- α -hydroxyacrylic acid is a water-soluble salt selected from the group consisting of sodium, potassium, ammonium, monoethanolamine and diethanolamine salts.
4. A washability improver as set forth in claim 1, wherein the salt of acrylic acid, methacrylic acid or maleic acid is a water-soluble salt selected from the group consisting of sodium, potassium, ammonium, monoethanolamine and diethanolamine salts.
5. A washability improver as set forth in claim 1, wherein the polymerization is carried out in the presence of a free-radical initiator selected from the group consisting of persulfates, redox type initiators, hydrogen peroxide, and water-soluble azo type initiators.
6. A washability improver as set forth in claim 5, wherein the free-radical initiator is used in an amount of 0.1 to 1.0 part by weight per 100 parts by weight of the monomeric acid or salt thereof are employed at a weight ratio of 10/1 to 1/10.
7. A washability improver as set forth in claim 1, wherein the poly- α -hydroxyacrylic acid or its salt and the monomeric acid or salt thereof are employed at a weight ratio of 10/1 to 1/10.
8. A washability improver as set forth in claim 1, wherein the polymerization is carried out at a temperature of 50 to 90 °C for 2 to 5 hours.
9. A washability improver as set forth in claim 1, wherein the polymerization is carried out by using an aqueous solution of the poly- α -hydroxyacrylic acid or its salt as a reaction medium.
10. A washability improver as set forth in claim 1, wherein the polymerization is carried out in the presence of a chain transfer agent.

(19)



Europäisches Patentamt
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(11) Publication number:

0 414 228 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **90116097.8**

(51) Int. Cl.⁵: **C11D 3/37, D06L 3/02,
D06L 1/14, D06M 11/38,
C08F 265/02**

(22) Date of filing: **22.08.90**

(30) Priority: **25.08.89 JP 217534/89**

(43) Date of publication of application:
27.02.91 Bulletin 91/09

(94) Designated Contracting States:
CH DE FR GB LI

(88) Date of deferred publication of the search report:
19.11.92 Bulletin 92/47

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(54) **Washability improver for textile article.**

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EP 0 414 228 A3



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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 6097

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-3 423 452 (SANDOZ) * examples * ---	1-4	C1103/37 D06L3/02 D06L1/14 D06M11/38 C08F265/02
X	FR-A-2 342 265 (SOLVAY & CIE) * page 2, line 35 - line 36; example 3 * ---	1-4	
X	FR-A-2 303 075 (SOLVAY & CIE) * page 2, line 25 - line 27; claims; examples * ---	1-4	
A	DE-B-2 814 354 (BASF) * examples * ---	1	
A	CHEMICAL ABSTRACTS, vol. 77, no. 18, 30 October 1972, Columbus, Ohio, US; abstract no. 115095, ' & JP-A-7213775 ' page 16 ; column 1 ; * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C110 D06L D06M C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 SEPTEMBER 1992	Examiner PFANNENSTEIN H.
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